

## **Determining point charge arrays that produce accurate ionic crystal fields for atomic cluster calculations**

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In performing atomic cluster calculations of local electronic structure defects in ionic crystals, the crystal is often modeled as a central cluster of 5 to 50 ions embedded in an array of point charges. For most crystals, however, a finite three-dimensional repeated array of unit cells generates electrostatic potentials that are in significant disagreement with the Madelung (infinite crystal) potentials computed by the Ewald method. This is illustrated for the cubic crystal  $\text{CaF}_2$ . We present a novel algorithm for solving this problem for any crystal whose unit cell information is known: (1) the unit cell is used to generate a neutral array containing typically 10,000 point charges at their normal crystallographic positions; (2) the array is divided into zone 1 (a volume defined by the atomic cluster of interest), zone 2 (several hundred additional point charges that together with zone 1 fill a spherical volume), and zone 3 (all other point charges); (3) the Ewald formula is used to compute the site potentials at all point charges in zones 1 and 2; (4) a system of simultaneous linear equations is solved to find the zone 3 charge values that make the zone 1 and zone 2 site potentials exactly equal to their Ewald values and the total charge and dipole moments equal to zero, and (5) the solution is checked at 1000 additional points randomly chosen in zone 1. The method is applied to 33 different crystal types with 50 to 71 ions in zone 1. In all cases the accuracy determined in step 5 steadily improves as the sizes of zones 2 and 3 are increased, reaching a typical rms error of 1  $\mu\text{V}$  in zone 1 for 500 point charges in zone 2 and 10,000 in zone 3.

**Keywords:** Crystal cluster calculations; Madelung potential; crystal field potential; Ewald potential; Madelung constant.

## 1. Introduction

In performing atomic cluster calculations of local electronic structure defects in ionic crystals, the crystal is often modeled as a central cluster of ions embedded in an array of point charges designed to reproduce the electrostatic field produced by the rest of the crystal. As has been pointed out in the literature, electrostatic potentials computed over a finite volume of an infinite periodic crystal lattice can lead to serious errors, and these errors do not necessarily diminish as the volume is increased. This computational problem was cleverly solved by Ewald in 1921<sup>1</sup>.

For some crystals, the standard crystallographic unit cell has zero electric dipole moment and small values of higher electrostatic moments; an array built from these unit cells will provide potentials in good agreement with the Madelung potentials for the infinite crystal computed by the Ewald summation method (described in Appendix B). Examples are the cubic crystals NaCl, KMgF<sub>3</sub>, MgO, and SrTiO<sub>3</sub>. However, most crystals have unit cells with significant electrostatic moments, and even a large array of these unit cells can yield inaccurate potential values<sup>2,3</sup>. The Evjen method<sup>4</sup> can be used to symmetrize ions on the corners, edges, and faces of the unit cell. However, only if the resulting unit cell has zero dipole moment is the sum unconditionally convergent, and even then a correction term is required in most cases<sup>5</sup>.

We have considered a number of approaches for obtaining point charge arrays that generate the Madelung potential using the crystal CaF<sub>2</sub> as an example. These include (1) using a large array of standard unit cells, (2) using a large array of Evjen unit cells, (3) using an array of point charges designed to mimic the space terms in the Ewald summation, and (4) placing point charges at fixed locations outside the cluster volume and solving a set of simultaneous linear equations to determine the optimal charge values. These investigations are reviewed in section 2.

In section 3 we describe an improved method designed to reproduce accurately the Madelung potential within any atomic cluster for any crystal whose unit cell information is known. The method can be summarized in the following steps:

(1) A  $2N \times 2N \times 2N$  array of unit cells is used to generate an array containing typically 10,000 point charges at their normal crystallographic positions and with their ground-state ionic charges.

(2) The array is divided into zone 1 (a volume containing the atomic cluster of interest), zone 2 (additional ions that together with zone 1 fill a spherical volume), and zone 3 (all other point charges)

(3) The Ewald formula is used to compute the site potentials for all point charges in zones 1 and 2.

(4) A system of simultaneous linear equations is solved to find the zone 3 charge values that make the zone 1 and zone 2 site potentials exactly equal to their Ewald values and the total charge and dipole moment equal to zero.

(5) The solution is checked at 1000 randomly chosen points within zone 1.

We have applied our new method to 33 different crystals. The results are summarized in Section 4 and presented in more detail in Appendix A. They show that the method is capable of determining point charge arrays that can reproduce the Madelung potential within a cluster of 50 atoms to a typical rms accuracy of 1  $\mu$ V.

Appendix B reviews the Ewald method for computing the potential within an infinite, periodic array of point charges and presents it in a form that permits immediate implementation by a programmer who does not have a background in crystallography.

## 2. Various Approaches to Finding Point Charges that Generate the Madelung Potential

### Large arrays of standard unit cells

It might be thought that a sufficiently large array of unit cells would reproduce the crystal field closely, at least in the center of the array. However, most crystals have unit cells with non-zero dipole moment and this produces a component to the electric field that (1) varies linearly with position, in violation of the periodic crystal symmetry, and (2) is not reduced by increasing the number of unit cells in the array. The reason for the latter is that the dipole field is produced by unbalanced charges at the outer surfaces of the array, which can be thought of as charge pairs separated by a distance  $R$ , the size of the array. If the array is increased in size, the field produced by each charge pair falls off as  $R^{-2}$ , but the number of charges at the surfaces grows as  $R^2$ , resulting in a constant field gradient.

As an example, consider the cubic crystal  $\text{CaF}_2$ . It has a 12-ion unit cell, with fractional coordinates given in Table I. To convert to Cartesian coordinates, multiply all values by 5.453 Å. The full crystal lattice is generated by translating this unit cell in  $x$ ,  $y$ , and  $z$  by integer multiples of the lattice constant 5.453 Å.

**Table I.** Location of ions in the standard  $\text{CaF}_2$  unit cell

Ion	$u_1, u_2, u_3$	$u_1, u_2, u_3$	$u_1, u_2, u_3$	$u_1, u_2, u_3$
Ca	0.00, 0.00, 0.00	0.00, 0.50, 0.50	0.50, 0.00, 0.50	0.50, 0.50, 0.00
F	0.25, 0.25, 0.25	0.25, 0.25, 0.75	0.25, 0.75, 0.25	0.25, 0.75, 0.75
F	0.75, 0.25, 0.25	0.75, 0.25, 0.75	0.75, 0.75, 0.25	0.75, 0.75, 0.75

To test the asymptotic dependence of the electrostatic field on ion array size, we constructed  $2N \times 2N \times 2N$  arrays of these unit cells ( $96 N^3$  ions) with increasing values of  $N$ . For each value of  $N$  the electrostatic potentials  $V(\mathbf{r}_k)$  at 1000 random points<sup>6</sup>  $\mathbf{r}_k$  within a central volume containing 51 ions was computed, where  $V(\mathbf{r}_k)$  is given by Eq. (1) and  $N_T = 96N^3$ .

$$V(\mathbf{r}_k) = \sum_{i=1}^{N_T} \frac{q_i}{|\mathbf{r}_k - \mathbf{r}_i|} \quad (1)$$

This potential is compared with the corresponding Madelung potentials  $V_E(\mathbf{r}_k)$  computed by the Ewald summation method (Appendix B). The deviation between these two potentials is given by

$$(\mathbf{r}_k) = V(\mathbf{r}_k) - V_E(\mathbf{r}_k) \quad (2)$$

The average deviation between the potentials is calculated as

$$\text{ave} = \frac{1}{1000} \sum_{k=1}^{1000} (\mathbf{r}_k) \quad (3)$$

and the rms variation of the deviations about their average is calculated as

$$\text{rms} = \sqrt{\frac{1}{1000} \sum_{k=1}^{1000} [(\mathbf{r}_k) - \text{ave}]^2}. \quad (4)$$

Table II shows that the overall shift in the electrostatic field  $\text{ave}$  and the rms error  $\text{rms}$  about that shifted value quickly reach asymptotic limits for arrays of only a few thousand ions. Adding additional layers of unit cells does not significantly change the potential at the 1000 random points<sup>6</sup> calculated using Eq (1).

**Table II** Average and rms deviations between eq (1) and Ewald potentials at 1000 random points<sup>6</sup> for  $2N \times 2N \times 2N$  arrays of  $\text{CaF}_2$  unit cells.

Unit cell array	Number of ions	$\text{ave}$ (eV)	$\text{rms}$ (eV)
4 x 4 x 4	768	-8.432	17.171
10 x 10 x 10	12,000	-8.484	17.262
20 x 20 x 20	96,000	-8.492	17.276
44 x 44 x 44	1,022,208	-8.494	17.280
120 x 120 x 120	20,736,000	-8.495	17.281

### Large arrays of Evjen unit cells

It is possible to eliminate the dipole moment of the  $\text{CaF}_2$  unit cell in Table I by distributing the corner and face atoms over all equivalent symmetry points. The resulting Evjen unit cell has zero dipole moment; the ion coordinates are listed in Table III.

**Table III.** Location of ions in the Evjen  $\text{CaF}_2$  unit cell

Ion	$u_1, u_2, u_3$	$u_1, u_2, u_3$	$u_1, u_2, u_3$	$u_1, u_2, u_3$
1/8 Ca	0.00, 0.00, 0.00	0.00, 0.00, 1.00	0.00, 1.00, 0.00	0.00, 1.00, 1.00
1/8 Ca	1.00, 0.00, 0.00	1.00, 0.00, 1.00	1.00, 1.00, 0.00	1.00, 1.00, 1.00
1/2 Ca	0.00, 0.50, 0.50	0.50, 0.00, 0.50	0.00, 0.50, 0.50	
1/2 Ca	1.00, 0.50, 0.50	0.50, 1.00, 0.50	1.00, 0.50, 0.50	
F	0.25, 0.25, 0.25	0.25, 0.25, 0.75	0.25, 0.75, 0.25	0.25, 0.75, 0.75
F	0.75, 0.25, 0.25	0.75, 0.25, 0.75	0.75, 0.75, 0.25	0.75, 0.75, 0.75

Evaluating Equation 1 for a  $4 \times 4 \times 4$  array of Evjen unit cells shows that for a central 51-atom  $\text{CaF}_2$  cluster the central 19 Ca ions have site potentials that are nearly the same with an average value of  $-28.2$  eV and the 32 F ions have an average site potential of  $2.5$  eV. These are both  $8.3$  eV lower than the values obtained by applying the Ewald method (described in Appendix B), which are  $-19.9792$  V for Ca and  $+10.7496$  V for F. Similar values occur when larger arrays are used. Table IV shows the average error in the electrostatic field  $\text{ave}$  and the rms variation  $\text{rms}$  about that average value for 1000 random points<sup>6</sup> within the central 51 ion cluster. Comparison with Table II shows that the elimination of the unit cell dipole moment greatly reduces  $\text{rms}$  but has little effect on  $\text{ave}$ . Thus an array of Evjen  $\text{CaF}_2$  unit cells can reproduce the spatial shape of the crystal field accurately, but the potential is shifted by a large value which affects calculations involving ionization energy and electron affinity.

**Table IV.** Average and rms deviations between eq (1) and the Ewald potentials at 1000 random points<sup>6</sup> for  $2N \times 2N \times 2N$  arrays of  $\text{CaF}_2$  Evjen unit cells.

Unit cell array	Number of ions	$\text{ave}$ (eV)	$\text{rms}$ (eV)
$4 \times 4 \times 4$	1,408	$-8.265$	$6.29 \times 10^{-4}$
$10 \times 10 \times 10$	22,000	$-8.291$	$2.13 \times 10^{-6}$
$20 \times 20 \times 20$	176,000	$-8.295$	$3.34 \times 10^{-8}$
$44 \times 44 \times 44$	2,141,392	$-8.296$	$< 10^{-9}$
$120 \times 120 \times 120$	38,016,000	$-8.296$	$< 10^{-9}$

### Weighted point charge arrays

The Ewald summation method (Appendix B) evaluates the crystal field at a point  $\mathbf{r}$  as a spatial sum plus an inverse lattice sum. If  $\epsilon$  is sufficiently small, the inverse lattice sum can be neglected, leaving only the real space sum of an array of point charges, where each charge value  $q_i$  is weighted by  $\text{erfc}(\epsilon |\mathbf{r}_i - \mathbf{r}|)$ . Moreover, if  $\epsilon$  is so small that the difference between  $\text{erfc}(\epsilon |\mathbf{r}_i - \mathbf{r}|)$  and  $\text{erfc}(\epsilon |\mathbf{r}_i|)$  is small for all  $\mathbf{r}$  in a central region, then the crystal

field in that region can be approximated as a spatial sum over the array of point charges  $q_i$  weighted by  $\text{erfc}(|\mathbf{r}_i|)$ .

This results in a modified form for equation (1)

$$V(\mathbf{r}_k) = \sum_{i=1}^{N_T} \frac{q_i}{|\mathbf{r}_k - \mathbf{r}_i|}, \text{ where } q_i = q_i \text{erfc}(|\mathbf{r}_i|) \quad (5)$$

To test this idea, we first chose 1000 random points<sup>6</sup> within the central 51-ion  $\text{CaF}_2$  cluster. Then we chose a value of  $\epsilon$  and constructed a series of  $2N \times 2N \times 2N$  arrays of unit cells of increasing size. At each value of  $N$  the eq (5) potential was computed at the 1000 random points and compared with their Ewald values. The process was terminated when increasing the value of  $N$  by 1 changed both  $\epsilon_{\text{ave}}$  and  $\epsilon_{\text{rms}}$  by less than 1  $\mu\text{V}$ . The results (Table V) show very slow convergence as the  $\epsilon$  value is decreased, and that an impractically large number of point charges would be required to achieve an rms below 1 mV over the central 51-ion sphere. However, this result is important in that it provides a general analytic expression for a point charge array that reproduces the Madelung field with an error that approaches zero as  $\epsilon$  approaches zero. Because the difference between  $\text{erfc}(|\mathbf{r}_i - \mathbf{r}|)$  and  $\text{erfc}(|\mathbf{r}_i|)$  is zero at  $\mathbf{r} = 0$ , the error decreases for decreasing cluster size. Note that Table V is the same for the standard  $\text{CaF}_2$  unit cell and the Evjen unit cell because the Gaussian shielding eliminates the surface dipole layers.

**Table V.** Averages and rms deviations between eq (1) and the Ewald potentials for  $\text{erfc}(|\mathbf{r}|)$ -weighted ionic charges at 1000 random points<sup>6</sup> within the central 51-ion cluster in the crystal  $\text{CaF}_2$

	Unit cell array	Number of ions	$\epsilon_{\text{ave}}$ (eV)	$\epsilon_{\text{rms}}$ (eV)
0.05	24 x 24 x 24	165,888	+0.41	4.08
0.03	38 x 38 x 38	658,464	+0.25	2.48
0.02	54 x 54 x 54	1,889,568	+0.16	1.66
0.015	70 x 70 x 70	4,116,000	+0.12	1.25
0.010	102 x 102 x 102	12,734,496	+0.080	0.831
0.005	220 x 220 x 220	127,776,000	-0.050	0.403

### Charge determination using simultaneous linear equations

Several previously published approaches for determining optimized point charge arrays have used a fixed array of point charges at their normal lattice positions<sup>7</sup> or on spherical surfaces<sup>8</sup>. In reference 7 the authors optimized the point charge values for six crystal types and report a worst case rms error of 0.1 kcal/mole (4.3 mV), but do not provide details on the size of the point charge array or the number of linear equations. In reference 8 the authors define intersecting spherical surfaces surrounding the atoms of the cluster, divide

the surfaces into several hundred surface elements, place a point charge at the center of each surface element, and solve a set of linear equations to determine the charge values that produce the correct (Ewald) potentials at those same points. These equations determine the same number of unknown charge values as known potentials and do not constrain the total charge or dipole moment to be zero. These authors found that the final accuracy was significantly improved by choosing an initial array that resulted in a neutral solution. Their best results were 0.17 mV rms error for the NaCl crystal and 2.2 mV rms error for  $(\text{Si}_3\text{O}_4)^{4+}$  in the faujasite structure.

### 3. An Improved Method for Determining Optimized Point Charges

We sought an improved method that could automatically determine a point charge array that would reproduce the Madelung potential within any chosen cluster of atoms for any crystal whose unit cell information is known, and that would not require manual intervention to modify the unit cell, to design surface segments, or to make the final total charge zero. After some consideration and experimentation, we concluded that:

(1) As presented in references 7 and 8, varying only the point charge values and not their positions allows a rapid solution by linear methods. We found that a good choice for the point charge positions was at their normal crystallographic coordinates. Placement on a sphere or at random points in space resulted in significantly poorer solutions.

(2) Much better accuracy is obtained within the atomic cluster (zone 1) if it is surrounded by point charges (zone 2) whose values are not varied and whose site potentials are included in the system of linear equations that determine the values of the outer (zone 3) point charges.

(3) It is only necessary to include the site potentials of the zone 1 and zone 2 ions in the equations. The accuracy within zone 1 is not improved when the potentials at other points within zone 1 are included in the equations.

(4) As the sizes of zones 2 and 3 are increased, the accuracy at a large number of points randomly chosen within zone 1 improves in a systematic way.

In detail, the method involves five steps.

#### Step 1

Compute the Cartesian space coordinates for a  $2N \times 2N \times 2N$  array of unit cells.

$$\begin{aligned} \mathbf{r}_{n,i_1,i_2,i_3} &= (u_{1,n} + i_1)\mathbf{a}_1 + (u_{2,n} + i_2)\mathbf{a}_2 + (u_{3,n} + i_3)\mathbf{a}_3 \\ &= \begin{pmatrix} x_{n,i_1,i_2,i_3} & y_{n,i_1,i_2,i_3} & z_{n,i_1,i_2,i_3} \end{pmatrix} \end{aligned} \quad (6)$$

The fractional unit cell coordinates for the  $n$ th ion in the unit cell are  $(u_{1,n} \ u_{2,n} \ u_{3,n})$ . The unit cell translation indices  $i_1$ ,  $i_2$ , and  $i_3$  vary from  $-N$  to  $N-1$  so that the volume of the unit cell array is centered at  $(0 \ 0 \ 0)$ . The index  $n$  varies over the ions of the unit cell, from 1 to  $n_{\text{max}}$ . The total number of ions is  $N_T = 8 \ N^3 \ n_{\text{max}}$ . The translation vectors  $\mathbf{a}_j$  describe the principal axes of the unit cell in Cartesian  $(x \ y \ z)$  coordinates.

$$\mathbf{a}_j = (a_{jx} \ a_{jy} \ a_{jz}), \quad j = 1, 2, 3 \quad (7)$$

The charge values are given by

$$q_{n,i_1,i_2,i_3} = q_n \quad (8)$$

### Step 2

The array generated in step 1 is divided into zone 1 (the central region containing the  $N_1$  ions of the atomic cluster of interest), zone 2 ( $N_2$  additional ions that together with zone 1 fill a spherical volume), and zone 3 (the  $N_3$  other point charges). The coordinates and charge values are  $\mathbf{r}_i$  and  $q_i$ , where  $i = 1$  to  $N_1$  for zone 1,  $i = N_1 + 1$  to  $N_C$  for zone 2 and  $i = N_C + 1$  to  $N_T$  for zone 3.  $N_C = N_1 + N_2$  and  $N_T = N_1 + N_2 + N_3$ .

### Step 3

The Ewald formula (Appendix B) is used to compute the site potentials  $V_E(\mathbf{r}_k)$  for all point charges in zones 1 and 2.

### Step 4

A set of linear equations is solved<sup>9</sup> that (1) makes  $V(\mathbf{r}_k)$  (Eq 6) equal to the Ewald values over zones 1 and 2 and (2) makes the charge and electric dipole moment of the total array equal to zero.

There are  $N_C = N_1 + N_2$  equations that make the site potentials  $V(\mathbf{r}_k)$  of the ions in zones 1 and 2 equal to their Ewald values:

$$\sum_{i=1}^{N_T} \frac{q_i + q_i}{|\mathbf{r}_k - \mathbf{r}_i|} = V_E(\mathbf{r}_k) \quad k = 1 \text{ to } N_1 + N_2 \quad (9)$$

$$q_i = 0 \quad i = 1 \text{ to } N_1 + N_2$$

The charge neutrality equation is:

$$\sum_{i=1}^{N_T} q_i + \sum_{i=N_C+1}^{N_T} q_i = 0 \quad (10)$$

The three dipole equations are:

$$\sum_{i=1}^{N_T} (q_i + q_i) \mathbf{r}_i = 0 \quad (11)$$

These  $N_1 + N_2 + 4$  equations are solved for the  $N_3$  charge value changes  $q_i$ , where  $i = N_1 + N_2 + 1$  to  $N_1 + N_2 + N_3$ . Since  $N_3 > N_1 + N_2 + 4$  (i.e. there are more parameters

than equations), the minimum norm solution is chosen. The solution is thus the array generated in step 1 where the zone 3 charge values have been modified by  $q_i$ .

### Step 5

To check the solution, the average and rms deviations ( $\sigma_{\text{ave}}$  and  $\sigma_{\text{rms}}$  in eqs 4 and 5) between the lattice potentials  $V(\mathbf{r}_k)$  (Eq 1) and the Ewald potentials  $V_E(\mathbf{r}_k)$  (Appendix B) are computed for 1000 random points<sup>6</sup> within zone 1.  $V_{\text{rms}}$  is the combined rms deviation between  $V(\mathbf{r}_k)$  and  $V_E(\mathbf{r}_k)$ , given by

$$V_{\text{rms}} = \sqrt{\sigma_{\text{ave}}^2 + \sigma_{\text{rms}}^2} = \sqrt{\frac{1}{1000} \sum_{k=1}^{1000} [V(\mathbf{r}_k) - V_E(\mathbf{r}_k)]^2} \quad (12)$$

## 4. Results

An example of the application of this method to the crystal  $\text{CaF}_2$  is shown in Table VI for four values of  $N_C$  and for three values of  $N_T$ . The  $V_{\text{rms}}$  error (eq 12) at 1000 random points in zone 1 decreases as  $N_C$  and  $N_T$  are increased, reaching 0.12  $\mu\text{V}$  for  $N_C = 514$  and  $N_T = 20,736$ . Several values were repeated a number of times to estimate the statistical variation due to the random selection of the 1000 points at which the solution was checked. The rms uncertainties are approximately 10% of  $V_{\text{rms}}$ .

**Table VI.** rms deviation (mV) at 1000 random points in zone 1 for the crystal  $\text{CaF}_2$  ( $N_1 = 62$ ).

$N_T$	$N_C = 62$	110	218	514
2,592	120	10.3	0.146	0.000312
6,144	107	9.14	0.141	0.000150
20,736	98.2	7.54	0.137	0.000123

The above method was applied to 33 crystals of varying symmetries to illustrate its versatility and accuracy. Appendix A contains tables of  $V_{\text{rms}}$  for  $N_1 = 50$  and several values of  $N_C = N_1 + N_2$  and  $N_T = N_1 + N_2 + N_3$  for each crystal. In all cases the accuracy determined in step 5 steadily improves as the  $N_C$  and  $N_T$  are increased, reaching a typical rms error of 1  $\mu\text{V}$  in zone 1 for  $N_C = 500$  and  $N_T = 10,000$ . These results are summarized in Table VII for  $N_1 = 50$  and  $N_C = 500$ .

As an example, for  $\text{CaF}_2$  with  $N_C = 514$  and  $N_T = 20,736$  the computer code requires 72 MBytes of memory and 9.7 minutes of computation time on a 450 MHz Pentium II processor, mostly in step 4.

**Table VII.** Summary of results for 33 crystals for atomic cluster with  $N_1 = 50$ , and  $N_C = 500$ .  $V_{\text{rms}}$  is the rms deviation between the field produced by the point charges determined by the method described in Section 3 and their Ewald values.

Crystal	$N_T$	$V_{\text{rms}}$ ( $\mu\text{V}$ )	Crystal	$N_T$	$V_{\text{rms}}$ ( $\mu\text{V}$ )
$\text{Al}_2\text{O}_3$	30,000	0.013	$\text{MgO}$	21,952	<0.001
$\text{AlPO}_4$	18,000	1.57	$\text{MgAl}_2\text{O}_4$	12,096	0.449
$\text{BeAl}_2\text{O}_4$	28,000	0.534	$\text{NaI}$	1,728	<0.001
$\text{Bi}_4\text{Ge}_3\text{O}_{12}$	16,416	0.114	$\text{NaNO}_3$	30,000	0.194
$\text{Bi}_{12}\text{GeO}_{20}$	14,256	0.151	$\text{PbMgF}_6$	24,000	0.216
$\text{CaCO}_3$	30,000	0.145	$\text{PbF}_4$	27,440	0.019
$\text{CaF}_2$	20,736	0.123	$\text{PbWO}_4$	24,000	0.240
$\text{CdWO}_4$	20,736	0.863	$\text{SiO}_2$	24,696	0.909
$\text{CsI}$	21,296	0.017	$\text{SrTiO}_3$	20,480	0.005
$\text{Gd}_2\text{SiO}_5$	32,000	0.014	$\text{Y}_2\text{O}_3$	17,280	0.297
$\text{KMgF}_3$	20,480	<0.001	$\text{YAlO}_3$	20,000	0.449
$\text{La}_2\text{O}_3$	20,480	0.244	$\text{YVO}_4$	24,000	0.936
$\text{LaF}_3$	24,000	0.287	$\text{Y}_2\text{OS}_2$	20,000	0.014
$\text{LiCaAlF}_6$	18,000	0.219	$\text{ZnO}$	23,328	0.334
$\text{Li}_2\text{PbO}_3$	24,000	0.763	$\text{ZnS}$	21,952	0.323
$\text{Lu}_3\text{Al}_5\text{O}_{12}$	34,560	0.513	$\text{Zn}_2\text{SiO}_4$	27,216	0.006
$\text{MgF}_2$	24,576	0.180			

## 5. Comments

The method described here is able to determine point charge arrays that reproduce the infinite crystal Madelung potential to an arbitrary mathematical accuracy throughout a chosen volume of space for a large variety of crystals. However, several factors can make the field within a physical crystal differ from the values computed by the Ewald summation formulas: (1) the arrangement of ions on the surface of a finite crystal may not produce the same internal field as the rest of the infinite crystal, (2) the physical crystal may have a variety of defects, (3) the unit cell coordinates may be inaccurate, and (4) atom charges may not be equal to their fully ionized values.

In the last case, if a ground-state molecular orbital calculation determines that the central cluster atoms do not have their fully ionized formal charges, then the Madelung potentials need to be recalculated using the atomic charges in the unit cell, and a new array of point charges found and used in a new molecular orbital calculation. This process is repeated until the atom charges are equal to the corresponding unit cell charges. When calculating clusters with partially ionized atoms, it is also important to control the charge state of the cluster by using a complete number of formula units.

The method described takes advantage of the ability of all quantum chemistry programs to evaluate the matrix elements for point charges such as nuclei. More rigorous approaches that include the Ewald potential in the matrix elements have been described<sup>10,11</sup> but have not been implemented in existing quantum chemistry codes.

The computer codes used in this work may be obtained from the web address [cfi.lbl.gov/instrumentation](http://cfi.lbl.gov/instrumentation).

## **Acknowledgments**

We thank P. Hughett, G. Hummer, R. Metzger, R. Martin, W. Moses, D. Templeton, J. Torrance, and A. Toukmaji for helpful discussions.

This work was supported in part by the Director, Office of Science, Office of Biological and Environmental Research, Medical Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and in part by Public Health Service Grant No. R01 CA48002, awarded by the National Cancer Institute, Department of Health and Human Services.

One of the authors (M.K.) would like to acknowledge grants from the Swedish Natural Science Research Council, and by Uppsala University, Faculty of Science and Technology (Collaboration with University of California at Berkeley and Cambridge University).

## Appendix A Other Crystal Types

In the sections below, 33 different crystal types are described in terms of their space group, symmetry, lattice parameters, and Madelung constant. For each crystal example  $x$ , Table A1. $x$  lists the non-equivalent atoms, their formal ionic charges ( $q$ ), the number per unit cell ( $M$ ), their fractional unit cell coordinates ( $u_1, u_2, u_3$ ), and their site potentials  $V_E$  (in volts) computed by the Ewald method (Appendix B). Table A2. $x$  lists the rms deviation  $V_{\text{rms}}$  (in mV) between the potentials at 1000 random points<sup>6</sup> within zone 1 and their Ewald values after the charge values in zone 3 have been adjusted to make all zone 1 and zone 2 site potentials equal to their Ewald values.

$$V_{\text{rms}} = \sqrt{\frac{1}{1000} \sum_{k=1}^{1000} [V(\mathbf{r}_k) - V_E(\mathbf{r}_k)]^2} \quad V(r_k) = \sum_{i=1}^{N_T} \frac{q_i}{|\mathbf{r}_k - \mathbf{r}_i|} \quad (\text{A1})$$

In the examples below, zone 1 is the smallest sphere centered at 0, 0, 0 that contains at least 50 ions.  $N_1$  is the number of ions in zone 1 and is between 50 and 71. Zone 2 is a spherical shell surrounding zone 1 and contains  $N_2$  additional ions. Zone 3 contains the remaining  $N_3$  ions. In the tables below,  $N_C = N_1 + N_2$  and  $N_T = N_1 + N_2 + N_3$ . Note that  $N_C$  is the number of ion site potentials used to determine the charge values in zone 3.

For six examples ( $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{SrTiO}_3$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{ZnO}$ ) the site potentials computed here are compared with those of reference 12. Agreement is excellent and slight differences are due to variations in the unit cells used.

The Madelung constant  $M$  appears often in the literature and is the binding energy of a formula unit divided by twice the binding energy of charges  $+e$  and  $-e$  at a characteristic distance  $R_0$  for the crystal, usually the distance between the closest pair of ions of different sign, and given by

$$M(R_0) = \frac{R_0}{28.79952} \sum_{k=1}^N f_k q_k V_E(\mathbf{r}_k), \quad (\text{A2})$$

where  $f_k$  is the number of ions of type  $k$  in the formula unit,  $q_k$  is in units of the electron charge,  $R_0$  is in units of Å, and  $V_E(\mathbf{r}_k)$  is in units of V. For five examples ( $\text{Al}_2\text{O}_3$ ,  $\text{CaF}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{MgF}_2$ ,  $\text{SiO}_2$ ) the Madelung constants computed here are compared with the values given in reference 13. Agreement is excellent and slight differences are due to variations in the unit cells used.

### Example 1: $\text{Al}_2\text{O}_3$

Space group 167: R -3 c; Symmetry trigonal

Lattice parameters  $a = b = 4.763$  Å,  $c = 13.000$  Å,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 24.3259 for  $R(\text{Al-O}) = 1.8562$  Å.

(Reference 13 lists 24.242 for  $R(\text{Al-O}) = 1.8478$  Å.)

Table A1.1 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Al	3	12	0.0000	0.0000	0.3522	-36.5483 (-36.587)*
O	-2	18	0.3064	0.0000	0.2500	26.3575 (26.390)*

\* Values in parenthesis from reference 12.

Table A2.1 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 52$ )

$N_T$	$N_C = 52$	100	208	500
1,920	119.	29.9	51.2	229.
6,480	12.6	2.11	0.169	0.00296
30,000	2.01	0.227	0.00458	0.000013

### Example 2: $AlPO_4$

Space group 152 : P 31 2 1; Symmetry trigonal

Lattice parameters  $a = b = 4.9420 \text{ \AA}$ ,  $c = 10.9450 \text{ \AA}$ ,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 34.2373 for  $R(P-O1) = 1.4913 \text{ \AA}$

Table A1.2 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Al	3	3	0.4661	0.0000	0.3333	-36.0361
P	5	3	0.4667	0.0000	0.8333	-60.1897
O1	-2	6	0.4126	0.2947	0.4007	31.7952
O2	-2	6	0.4128	0.2572	0.8816	31.2316

Table A2.2 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 50$ )

$N_T$	$N_C = 50$	100	200	502
1,152	510	101	421	131
3,888	486	36.7	1.41	0.187
18,000	390	44.7	1.19	0.00157

### Example 3: $BeAl_2O_4$

Space group 62 : P n m a; Symmetry orthorhombic

Lattice parameters  $a = 9.4020 \text{ \AA}$ ,  $b = 5.4750 \text{ \AA}$ ,  $c = 4.4260 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000^\circ$

Madelung constant 26.7873 for  $R(Be-O1) = 1.5661 \text{ \AA}$

Table A1.3 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Be	2	4	0.0928	0.2500	0.4339	-29.6640
Al1	3	4	0.0000	0.0000	0.0000	-35.5409
Al2	3	4	0.2728	0.2500	0.9949	-36.6267
O1	-2	4	0.0903	0.2500	0.7877	28.2541
O2	-2	4	0.4330	0.2500	0.2414	27.4711
O3	-2	8	0.1633	0.0154	0.2569	26.3300

Table A2.3 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 51$ )

$N_T$	$N_C = 51$	105	201	500
1,792	363	62.8	8.40	52.1
6,048	352	37.8	0.572	0.00112
28,000	245	31.3	0.364	0.000534

#### Example 4: $\text{Bi}_4\text{Ge}_3\text{O}_{12}$

Space group 220: I -4 3 d; Symmetry cubic

Lattice parameters  $a = b = c = 10.5240 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000$

Madelung constant 90.5205 for  $R(\text{Ge-O}) = 1.7501 \text{ \AA}$

Table A1.4 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Bi	3	16	0.0875	0.0875	0.0875	-30.1645
Ge	4	12	0.3750	0.0000	0.2500	-45.6327
O	-2	48	0.0695	0.1267	0.2877	24.1679

Table A2.4 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 50$ )

$N_T$	$N_C = 50$	102	202	501
4,864	119.	10.5	0.336	0.000246
16,416	114.	11.9	0.265	0.000114

#### Example 5: $\text{Bi}_{12}\text{GeO}_{20}$

Space group 197: I 2 3; Symmetry cubic

Lattice parameters  $a = b = c = 10.1530 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000$

Madelung constant 127.4590 for  $R(\text{Ge-O3}) = 1.7638 \text{ \AA}$

Table A1.5 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Bi	3	24	0.1758	0.3185	0.0159	-29.9730
Ge	4	2	0.0000	0.0000	0.0000	-42.1754
O1	-2	24	0.1348	0.2513	0.4859	19.4117
O2	-2	8	0.1943	0.1943	0.1943	19.9025
O3	-2	8	0.8997	0.8997	0.8997	26.0375

Table A2.5 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 61$ )

$N_T$	$N_C = 61$	101	205	507
4,224	48.7	5.65	0.389	0.000499
14,256	38.8	4.94	0.267	0.000151

### Example 6: $\text{CaCO}_3$

Space group 167:  $R\bar{3}c$ ; Symmetry trigonal

Lattice parameters  $a = b = 4.9910 \text{ \AA}$ ,  $c = 17.0620 \text{ \AA}$ ,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 20.2527 for  $R(\text{C-O}) = 1.2842 \text{ \AA}$

Table A1.6 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Ca	2	6	0.0000	0.0000	0.0000	-21.1561
C	4	6	0.0000	0.0000	0.2500	-56.1801
O	-2	18	0.2573	0.0000	0.2500	31.1936

Table A2.6 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 51$ )

$N_T$	$N_C = 51$	111	201	508
1,920	121	46.0	101	162
6,480	121	8.01	0.281	0.0420
30,000	276	6.40	0.426	0.000145

### Example 7: $\text{CaF}_2$

Space group 225:  $Fm\bar{3}m$ ; Symmetry cubic

Lattice parameters  $a = b = c = 5.453 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000^\circ$

Madelung constant 5.03879 for  $R(\text{Ca-F}) = 2.3612 \text{ \AA}$

Reference 13 lists 5.03879 for  $R(\text{Ca-F}) = 2.360352 \text{ \AA}$

Table A1.7 Non-equivalent atoms

Atom	q	$u_1$	$u_2$	$u_3$	$V_E(V)$
Ca	2	0.0000	0.0000	0.0000	-19.9792
F	-1	0.2500	0.2500	0.2500	10.7496

Table A2.7 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 62$ )

$N_T$	$N_C = 62$	110	218	514
2,592	120.	10.3	0.146	0.000312
6,144	107.	9.14	0.141	0.000150
20,736	98.2	7.54	0.137	0.000123

### Example 8: $\text{CdWO}_4$

Space group 13: P 12/c 1; Symmetry monoclinic

Lattice parameters  $a = 5.028 \text{ \AA}$ ,  $b = 5.862 \text{ \AA}$ ,  $c = 5.067 \text{ \AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 91.50^\circ$

Madelung constant 38.2524 for  $R(\text{W-O2}) = 1.7828 \text{ \AA}$

Table A1.8 Non-equivalent atoms

Atom	q	$M$	$u_1$	$u_2$	$u_3$	$V_E(V)$
Cd	2	2	0.5000	0.6977	0.2500	-25.6497
W	6	2	0.0000	0.1785	0.2500	-59.2878
O1	-2	4	0.2030	0.0980	0.9490	28.5372
O2	-2	4	0.2420	0.3720	0.3830	24.1892

Table A2.8 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 50$ )

$N_T$	$N_C = 50$	100	202	500
2,592	329	65.3	1.84	0.00247
6,144	333	52.7	1.34	0.00130
20,736	291	49.5	1.17	0.000863

### Example 9: $\text{CsI}$

Space group 221: P m -3 m; Symmetry cubic

Lattice parameters  $a = b = c = 4.5680 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000^\circ$

Madelung constant 1.7627 for  $R(\text{Cs-I}) = 3.9560 \text{ \AA}$

Table A1.9 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Cs	1	1	0.0000	0.0000	0.0000	-6.4161
I	-1	1	0.5000	0.5000	0.5000	6.4161

Table A2.9 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 51$ )

$N_T$	$N_C = 51$	113	229	531
1,024	10.3	0.247	0.0295	†
5,488	10.6	0.0471	0.0141	0.000024
21,296	10.6	0.0826	0.0114	0.000017

† underdetermined system, number of equations =  $N_C + 4 = 535$ , number of parameters =  $N_T - N_C = 493$

### Example 10: $Gd_2SiO_5$

Space group 14: P 21/c Symmetry monoclinic

Lattice parameters  $a = 9.1200 \text{ \AA}$ ,  $b = 7.0600 \text{ \AA}$ ,  $c = 6.7300 \text{ \AA}$ ,  $\alpha = 90.00^\circ$ ,  $\beta = 107.60^\circ$

Madelung constant 34.3842 for  $R(\text{Si-O4}) = 1.5959 \text{ \AA}$

Table A1.10 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Gd1	3	4	0.1145	0.1460	0.4163	-31.0448
Gd2	3	4	0.5246	0.6245	0.2343	-29.5590
Si	4	4	0.2020	0.5876	0.4598	-48.4458
O1	-2	4	0.2030	0.4302	0.6453	25.0875
O2	-2	4	0.1317	0.4587	0.2520	24.7592
O3	-2	4	0.3839	0.6361	0.5059	26.9557
O4	-2	4	0.0941	0.7681	0.4507	24.3877
O5	-2	4	0.3837	0.3782	0.0487	21.2586

Table A2.10 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 50$ )

$N_T$	$N_C = 50$	100	200	502
2,048	40.0	3.06	0.579	0.0874
6,912	10.5	1.62	0.0387	0.000052
32,000	4.85	0.602	0.0142	0.000014

### Example 11: $KMgF_3$

Space group 221: P m  $\bar{3}$  m; Symmetry cubic

Lattice parameters  $a = b = c = 3.9800 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000^\circ$

Madelung constant 6.1888 for  $R(\text{Mg-F}) = 1.9900 \text{ \AA}$

Table A1.11 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
K	1	1	0.0000	0.0000	0.0000	-9.7456
Mg	2	1	0.5000	0.5000	0.5000	-22.3911
F	-1	3	0.5000	0.5000	0.0000	11.6789

Table A2.11 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 51$ )

$N_T$	$N_C = 51$	111	209	517
1,080	1.36	0.120	0.200	1,347.
5,000	0.410	0.0383	0.000882	0.000003
20,480	0.146	0.0130	0.000269	<1.0e-6

### Example 12: $\text{La}_2\text{O}_3$

Space group 164: P -3 m 1; Symmetry trigonal

Lattice parameters  $a = b = 3.9380 \text{ \AA}$ ,  $c = 6.1360 \text{ \AA}$ ,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 24.1492 for  $R(\text{La-O1}) = 2.3653 \text{ \AA}$

(Reference 13 lists 24.179 for  $R(\text{La-O1}) = 2.3711 \text{ \AA}$ )

Table A1.12 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
La	3	2	0.3333	0.6667	0.2467	-29.0000
O1	-2	2	0.3333	0.6667	0.6471	20.1666
O2	-2	1	0.0000	0.0000	0.0000	19.6842

Table A2.12 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 51$ )

$N_T$	$N_C = 51$	111	201	502
1,080	189.	23.5	67.6	734.
5,000	199.	10.3	1.45	0.000427
20,480	180.	9.70	0.807	0.000244

### Example 13: $\text{LaF}_3$

Space group 165: P -3 c 1; Symmetry trigonal

Lattice parameters  $a = b = 7.1850 \text{ \AA}$ ,  $c = 7.3510 \text{ \AA}$ ,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 27.9922 for  $R(\text{La-F2}) = 2.4171 \text{ \AA}$

Table A1.13 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
La	3	6	0.6598	0.0000	0.2500	-27.2026
F1	-1	12	0.3659	0.0536	0.0813	9.6371
F2	-1	4	0.3333	0.6666	0.1859	10.2515
F3	-1	2	0.0000	0.0000	0.2500	10.3769

Table A2.13 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 50$ )

$N_T$	$N_C = 50$	100	208	504
1,536	88.4	25.4	0.600	2.08
5,184	76.2	21.9	0.372	0.000353
24,000	69.4	16.8	0.251	0.000287

#### Example 14: $\text{LiCaAlF}_6$

Space group 163: P -3 1 c; Symmetry trigonal

Lattice parameters  $a = b = 5.0070 \text{ \AA}$ ,  $c = 9.6420 \text{ \AA}$ ,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 14.2988 for  $R(\text{Al-F}) = 1.8044 \text{ \AA}$

Table A1.14 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Li	1	2	0.3333	0.6667	0.2500	-13.5070
Ca	2	2	0.0000	0.0000	0.0000	-19.4568
Al	3	2	0.6667	0.3333	0.2500	-32.3486
F	-1	12	0.3769	0.0311	0.1434	13.1252

Table A2.14 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 51$ )

$N_T$	$N_C = 51$	105	213	504
1,152	96.3	48.7	90.6	101.
3,888	103.	13.4	0.398	0.00640
18,000	122.	15.0	0.148	0.000219

#### Example 15: $\text{Li}_2\text{PbO}_3$

Space group 15: C 2/c; Symmetry monoclinic

Lattice parameters  $a = 5.4450 \text{ \AA}$ ,  $b = 9.2610 \text{ \AA}$ ,  $c = 5.4760 \text{ \AA}$ ,  $\alpha = \gamma = 90.00^\circ$ ,  $\beta = 111.20^\circ$

Madelung constant 23.4689 for  $R(\text{Li-O1}) = 2.0904 \text{ \AA}$

Table A1.15 Non-equivalent atoms

Atom	q	$M$	$u_1$	$u_2$	$u_3$	$V_E(V)$
Li1	1	4	0.0000	0.4268	0.2500	-15.1777
Li2	1	4	0.0000	0.7618	0.2500	-15.0677
Pb	4	4	0.0000	0.0897	0.2500	-38.3036
O1	-2	8	0.2381	0.0793	0.0135	23.3099
O2	-2	4	0.2500	0.2500	0.500	23.3179

Table A2.15 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 50$ )

$N_T$	$N_C = 50$	100	200	501
1,536	193	59.2	8.85	370
5,184	163	25.4	1.56	0.00315
24,000	183	15.1	0.762	0.000763

### Example 16: $\text{Lu}_3\text{Al}_5\text{O}_{12}$

Space group 220:  $I-43d$ ; Symmetry cubic

Lattice parameters  $a = b = c = 11.9060 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000$

Madelung constant 87.4746 for  $R(\text{Al}_2\text{-O}) = 1.7597 \text{ \AA}$

Table A1.16 Non-equivalent atoms

Atom	q	$M$	$u_1$	$u_2$	$u_3$	$V_E(V)$
Lu	3	24	0.1250	0.0000	0.2500	-31.0849
Al1	3	16	0.0000	0.0000	0.0000	-37.8197
Al2	3	24	0.3750	0.0000	0.2500	-36.8592
O	-2	96	0.9706	0.0537	0.1509	24.7180

Table A2.16 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 57$ )

$N_T$	$N_C = 57$	105	225	521
1,280	545	51.9	0.877	0.251
10,240	321	38.3	0.622	0.000601
34,560	364	32.4	0.577	0.000513

### Example 17: $\text{MgF}_2$

Space group 136:  $P4_2/mnm$ ; Symmetry tetragonal

Lattice parameters  $a = b = 4.628 \text{ \AA}$ ,  $c = 3.045 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000$

Madelung constant 4.7894 for  $R(\text{Mg-F}) = 1.9844 \text{ \AA}$

(Reference 13 lists 4.762 for  $R(\text{Mg-F}) = 1.9677 \text{ \AA}$ )

Table A1.17 Non-equivalent atoms

Atom	q	<i>M</i>	<i>u</i> <sub>1</sub>	<i>u</i> <sub>2</sub>	<i>u</i> <sub>3</sub>	<i>V</i> <sub>E</sub> (V)
Mg	2	2	0.0000	0.0000	0.0000	-22.0466
F	-1	4	0.3032	0.3032	0.0000	12.7071

Table A2.17 rms deviation (mV) at 1000 random points in zone 1 (*N*<sub>1</sub> = 51)

<i>N</i> <sub>T</sub>	<i>N</i> <sub>C</sub> = 51	101	201	500
1,296	229	26.4	6.65	178
6,000	207	23.6	0.531	0.000188
24,576	217	18.8	0.415	0.000180

### Example 18: MgO

Space group 225: F m -3 m; Symmetry cubic

Lattice parameters *a* = *b* = *c* = 4.2170 Å,  $\alpha = \beta = \gamma = 90.000^\circ$

Madelung constant 6.9903 for *R*(Mg-O) = 2.1085 Å

Table A1.18 Non-equivalent atoms

Atom	q	<i>M</i>	<i>u</i> <sub>1</sub>	<i>u</i> <sub>2</sub>	<i>u</i> <sub>3</sub>	<i>V</i> <sub>E</sub> (V)
Mg	2	4	0.0000	0.0000	0.0000	-23.8697 (-23.902)*
O	-2	4	0.5000	0.5000	0.5000	23.8697 (-23.902)*

\* Values in parenthesis from reference 12.

Table A2.18 rms deviation (mV) at 1000 random points in zone 1 (*N*<sub>1</sub> = 57)

<i>N</i> <sub>T</sub>	<i>N</i> <sub>C</sub> = 57	123	203	515
1,728	0.269	0.00870	0.00076	0.595
4,096	0.0878	0.00253	0.000241	0.000002
21,952	0.00888	0.000265	0.000028	<1.0e-6

### Example 19: MgAl<sub>2</sub>O<sub>4</sub>

Space group 227: F d 3 m; Symmetry cubic

Lattice parameters *a* = *b* = *c* = 8.0890 Å,  $\alpha = \beta = \gamma = 90.000^\circ$

Madelung constant 31.5872 for *R*(Al-O) = 1.9207 Å

Table A1.19 Non-equivalent atoms

Atom	q	<i>M</i>	<i>u</i> <sub>1</sub>	<i>u</i> <sub>2</sub>	<i>u</i> <sub>3</sub>	<i>V</i> <sub>E</sub> (V)
Mg	2	8	0.0000	0.0000	0.0000	-25.7734
Al	3	16	0.6250	0.6250	0.6250	-35.6216
O	-2	32	0.3873	0.3873	0.3873	26.0437

Table A2.19 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 58$ )

$N_T$	$N_C = 58$	106	216	500
3,584	156	12.5	0.0998	0.000425
12,096	142	9.08	0.0422	0.000449

### Example 20: NaI

Space group Fm 3m: Symmetry; cubic

Lattice parameters  $a = b = c = 6.470 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000$

Madelung constant 1.7476 for  $R(\text{Na-I}) = 3.2350 \text{ \AA}$

Table A1.20 Non-equivalent atoms

Atom	q	$M$	$u_1$	$u_2$	$u_3$	$V_E(\text{V})$
Na	1	4	0.0000	0.0000	0.0000	-7.7789
I	-1	4	0.5000	0.5000	0.5000	7.7789

Table A2.20 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 56$ )

$N_T$	$N_C = 56$	136	208	552
1,728	0.00235	0.000040	<1.0e-6	<1.0e-6
4,096	0.000720	0.000013	<1.0e-6	<1.0e-6
21,952	0.000074	<1.0e-6	<1.0e-6	<1.0e-6

### Example 21: $\text{NaNO}_3$

Space group 167: R -3 c; Symmetry trigonal

Lattice parameters  $a = b = 5.0700 \text{ \AA}$ ,  $c = 16.8200 \text{ \AA}$ ,  $\alpha = \beta = 90.000$ ,  $\gamma = 120.000$

Madelung constant 24.0255 for  $R(\text{N-O}) = 1.2569 \text{ \AA}$

Table A1.21 Non-equivalent atoms

Atom	q	$M$	$u_1$	$u_2$	$u_3$	$V_E(\text{V})$
Na	1	6	0.0000	0.0000	0.0000	-13.0920
N	5	6	0.0000	0.0000	0.2500	-65.1918
O	-2	18	0.2479	0.0000	0.2500	35.2450

Table A2.21 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 51$ )

$N_T$	$N_C = 51$	105	201	508
1,920	104	44.2	59.9	75.3
6,480	104	8.48	0.318	0.0107
30,000	108	8.30	0.462	0.000194

### Example 22: PbMgF<sub>6</sub>

Space group 148: R  $\bar{3}$ ; Symmetry trigonal

Lattice parameters  $a = b = 5.2500 \text{ \AA}$ ,  $c = 13.9600 \text{ \AA}$ ,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 17.7236 for  $R(\text{Mg-F}) = 1.9755 \text{ \AA}$

Table A1.22 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(\text{V})$
Mg	2	3	0.0000	0.0000	0.0000	-23.5986
Pb	4	3	0.0000	0.0000	0.5000	-34.5433
F	-1	18	0.3190	0.0180	-0.0800	12.1678

Table A2.22 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 55$ )

$N_T$	$N_C = 55$	103	207	500
1,536	104	21.9	51.7	60.5
5,184	79.9	8.05	0.439	0.00991
24,000	107	9.10	0.206	0.000216

### Example 23: PbF<sub>4</sub>

Space group 139: I 4/m m m; Symmetry tetragonal

Lattice parameters  $a = b = 4.2470 \text{ \AA}$ ,  $c = 8.0300 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000^\circ$

Madelung constant 13.2381 for  $R(\text{Pb-F}_2) = 1.9673 \text{ \AA}$

Table A1.23 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(\text{V})$
Pb	4	2	0.0000	0.0000	0.0000	-36.1738
F1	-1	4	0.0000	0.5000	0.0000	13.7528
F2	-1	4	0.0000	0.0000	0.2450	10.7937

Table A2.23 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 51$ )

$N_T$	$N_C = 51$	109	203	509
2,160	16.6	2.58	0.186	86.2
5,120	13.0	2.34	0.0388	0.000056
27,440	10.8	2.26	0.0333	0.000019

### Example 24: PbWO<sub>4</sub>

Space group 88: I 41/a; Symmetry tetragonal

Lattice parameters  $a = b = 5.5000 \text{ \AA}$ ,  $c = 12.1200 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000^\circ$

Madelung constant 37.1142 for PbWO<sub>4</sub> based on  $R(\text{W-O}) = 1.7531 \text{ \AA}$

Table A1.24 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Pb	2	4	0.5000	0.7500	0.1250	-23.7320
W	6	4	0.0000	0.2500	0.1250	-59.1325
O	-2	16	0.2210	0.4010	0.3890	25.9323

Table A2.24 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 52$ )

$N_T$	$N_C = 52$	100	202	500
1,536	238	34.3	2.28	24.8
5,184	247	20.8	0.527	0.00130
24,000	198	16.5	0.484	0.000240

### Example 25: SiO<sub>2</sub>

Space group 152: P 31 2 1; Symmetry trigonal

Lattice parameters  $a = b = 4.9650 \text{ \AA}$ ,  $c = 5.4240 \text{ \AA}$ ,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 17.6054 for SiO<sub>2</sub> based on  $R(\text{Si-O}) = 1.6014 \text{ \AA}$

(Reference 13 lists 17.609 for  $R(\text{Si-O}) = 1.6191 \text{ \AA}$ )

Table A1.25 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Si	4	3	0.5248	0.0000	0.3333	-48.3226 (-48.384)*
O	-2	6	0.1570	0.4160	-0.1232	30.8302 (30.803)*

\* Values in parenthesis from reference 12.

Table A2.25 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 50$ )

$N_T$	$N_C = 50$	100	202	500
1,944	525	69.7	1.81	0.280
4,608	811	59.5	1.28	0.00197
24,696	599	48.8	1.05	0.000909

### Example 26: SrTiO<sub>3</sub>

Space group 195: P 2 3; Symmetry cubic

Lattice parameters  $a = b = c = 3.8970 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000^\circ$

Madelung constant 24.7550 for  $R(\text{Ti-O}) = 1.9485 \text{ \AA}$

Table A1.26 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Sr	2	1	0.5000	0.5000	0.5000	-19.9063
Ti	4	1	0.0000	0.0000	0.0000	-45.7360 (-45.642)*
O	-2	3	0.5000	0.0000	0.0000	23.8552 (23.806)*

\* Values in parenthesis from reference 12.

Table A2.26 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 57$ )

$N_T$	$N_C = 57$	111	221	511
1,080	13.1	0.715	0.0528	†
5,000	4.36	0.181	0.00518	0.000016
20,480	1.69	0.0614	0.00184	0.000005

† poorly determined system, number of equations =  $N_C + 4 = 516$ , number of parameters =  $N_T - N_C = 569$

### Example 27: $Y_2O_3$

Space group 206:  $I a \bar{3}$ ; Symmetry cubic

Lattice parameters  $a = b = c = 10.6040 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000$

Madelung constant 49.4171 for  $R(Y1-O) = 2.2475 \text{ \AA}$

Table A1.27 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Y1	3	8	0.2500	0.2500	0.2500	-31.7976 *
Y2	3	24	0.9672	0.0000	0.2500	-30.5650 *
O	-2	48	0.3890	0.1540	0.3780	21.8968 (21.892)*

\* Values in parenthesis for O from reference 12 and the weighted average of the two non-equivalent Y sites is given as -31.113 V

Table A2.27 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 50$ )

$N_T$	$N_C = 50$	104	206	506
5,120	177	30.7	0.481	0.000395
17,280	153	29.6	0.381	0.000297

### Example 28: $YAlO_3$

Space group 62:  $P n m a$ ; Symmetry orthorhombic

Lattice parameters  $a = 5.3300 \text{ \AA}$ ,  $b = 7.3750 \text{ \AA}$ ,  $c = 5.1800 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000$

Madelung constant 22.9680 for  $R(Al-O1) = 1.9015 \text{ \AA}$

Table A1.28 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Y	3	4	0.0526	0.2500	0.9896	-30.3846
Al	3	4	0.0000	0.0000	0.5000	-38.1634
O1	-2	4	0.4750	0.2500	0.0860	23.9211
O2	-2	8	0.2930	0.0440	0.7030	23.5958

Table A2.28 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 50$ )

$N_T$	$N_C = 50$	100	200	500
1,280	279	48.3	2.10	11.2
4,320	238	28.4	1.46	0.000903
20,000	211	26.9	1.38	0.000449

### Example 29: $YVO_4$

Space group 141: I 41/a m d; Symmetry tetragonal

Lattice parameters  $a = b = 7.1180 \text{ \AA}$ ,  $c = 6.2890 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90.000$

Madelung constant 33.8944 for  $R(V-O) = 1.7086 \text{ \AA}$

Table A1.29 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Y	3	4	0.0000	0.7500	0.1250	-32.2259
V	5	4	0.0000	0.2500	0.3750	-53.1295
O	-2	16	0.0000	0.4342	0.2008	26.1235

Table A2.29 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 52$ )

$N_T$	$N_C = 52$	100	202	500
1,536	169	62.6	1.88	0.0890
5,184	143	46.1	1.34	0.00143
24,000	114	40.0	0.887	0.000936

### Example 30: $Y_2OS_2$

Space group 14: P 21/C; Symmetry monoclinic

Lattice parameters  $a = 8.2550 \text{ \AA}$ ,  $b = 6.8850 \text{ \AA}$ ,  $c = 6.8530 \text{ \AA}$ ,  $\alpha = \beta = 90.00$ ,  $\gamma = 99.600$

Madelung constant 21.9953 for  $R(Y_2O) = 2.2491 \text{ \AA}$

Table A1.30 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Y1	3	4	0.5760	0.6445	0.8209	-27.8063
Y2	3	4	0.1380	0.5546	0.7496	-26.9736
O	-2	4	0.3837	0.0855	0.3513	24.1274
S1	-2	4	0.6807	0.1327	0.0750	17.0612
S2	-2	4	0.0760	0.2766	0.0303	17.4645

Table A2.30 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 50$ )

$N_T$	$N_C = 50$	100	200	500
1,280	20.3	3.92	0.449	1.58
4,320	9.83	1.64	0.0589	0.000046
20,000	4.58	0.492	0.0231	0.000014

### Example 31: ZnO (hexagonal)

Space group 186: P 63 m c; Symmetry hexagonal

Lattice parameters  $a = b = 3.2420 \text{ \AA}$ ,  $c = 5.1880 \text{ \AA}$ ,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 6.5531 for  $R(\text{Zn-O}) = 1.9690 \text{ \AA}$

Table A1.31 Non-equivalent atoms

Atom	q	M	$u_1$	$u_2$	$u_3$	$V_E(V)$
Zn	2	2	0.3333	0.6667	0.0000	-23.9616 (-24.024)*
O	-2	2	0.3333	0.6667	0.3819	23.9616 (24.024)*

\* Values in parenthesis from reference 12.

Table A2.31 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 51$ )

$N_T$	$N_C = 51$	103	204	504
2,048	237	26.9	0.338	24.9
6,912	251	22.6	0.229	0.000416
23,328	239	19.2	0.215	0.000334

### Example 32: ZnS (cubic)

Space group 186: P 63 m c; Symmetry hexagonal

Lattice parameters  $a = b = 3.8230 \text{ \AA}$ ,  $c = 6.2610 \text{ \AA}$ ,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 6.5522 for  $R(\text{Zn-S}) = 2.3448 \text{ \AA}$

Table A1.32 Non-equivalent atoms

Atom	q	$M$	$u_1$	$u_2$	$u_3$	$V_E(V)$
Zn	2	4	0.3333	0.6667	0.0000	-20.1194
S	-2	4	0.3333	0.6667	0.3748	20.1194

Table A2.32 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 71$ )

$N_T$	$N_C = 71$	123	239	525
1,728	45.5	5.06	0.130	0.0444
4,096	56.1	4.19	0.0472	0.000455
21,952	56.9	3.10	0.0213	0.000323

### Example 33: $Zn_2SiO_4$

Space group 148: R  $\bar{3}$ ; Symmetry trigonal

Lattice parameters  $a = b = 14.27 \text{ \AA}$ ,  $c = 8.95 \text{ \AA}$ ,  $\alpha = \beta = 90.000^\circ$ ,  $\gamma = 120.000^\circ$

Madelung constant 55.8729 for  $R(Si-O_2) = 1.5837 \text{ \AA}$

Table A1.33 Non-equivalent atoms

Atom	q	$M$	$u_1$	$u_2$	$u_3$	$V_E(V)$
Zn1	2	18	0.2151	0.1920	0.5814	-24.3286
Zn2	2	18	0.2091	0.1917	0.9153	-24.0291
Si	4	18	0.2117	0.1956	0.2494	-48.1408
O1	-2	18	0.3220	0.3178	0.2490	27.6386
O2	-2	18	0.2056	0.1283	0.1036	28.0881
O3	-2	18	0.2092	0.1256	0.3926	27.2840
O4	-2	18	0.2164	0.1104	0.7495	26.3642

Table A2.33 rms deviation (mV) at 1000 random points in zone 1 ( $N_1 = 54$ )

$N_T$	$N_C = 54$	102	204	504
1,008	34.6	7.16	28.1	†
8,064	4.28	0.345	0.0126	0.000058
27,216	1.71	0.149	0.00455	0.000006

† poorly determined system, number of equations =  $N_C + 4 = 508$ , number of parameters =  $N_T - N_C = 504$

## Appendix B The Ewald Summation Method

The Ewald method for computing the binding energy  $W_k$  of an ion of charge  $q_k$  and position  $\mathbf{r}_k$  in an infinite periodic crystal lattice requires computing three quantities:

The first is  $W_k^r$ , the binding energy of the  $k$ th ion due to the infinite array of other ions of charge  $q_i$  and position  $\mathbf{r}_i$ , each shielded by a Gaussian charge distribution  $\exp(-|\mathbf{r}-\mathbf{r}_i|^2)$  having charge  $-q_i$ . Due to the shielding, this spatial sum converges rapidly.

The second is  $W_k^f$ , the binding energy of the  $k$ th ion due to the infinite array of Gaussian charge distributions described above plus an additional Gaussian distribution of charge  $-q_k$  at  $\mathbf{r}_k$ . Since this sum is over a complete, periodic array of identical Gaussian distributions, it can be evaluated in the Fourier (reciprocal lattice) space, where the sum is over a single Gaussian and converges rapidly.

The third is  $W_k^c$ , the binding energy of the  $k$ th ion due to the additional Gaussian charge distribution that was added in computing  $W_k^f$ .

These three terms are combined to compute the binding energy of the point charge  $q_k$ :

$$W_k = W_k^r - W_k^f + W_k^c$$

The Cartesian space coordinates  $\mathbf{r}_{n,i_1,i_2,i_3} = (x_{n,i_1,i_2,i_3} \ y_{n,i_1,i_2,i_3} \ z_{n,i_1,i_2,i_3})$  of the  $n$ th ion in the  $(i_1 \ i_2 \ i_3)$  unit cell can be computed from the fractional unit cell coordinates  $(u_{n1} \ u_{n2} \ u_{n3})$  and the three unit cell translation vectors  $\mathbf{a}_j$ , where

$$\mathbf{a}_j = (a_{jx} \ a_{jy} \ a_{jz}), \quad j = 1, 2, 3$$

$$\mathbf{r}_{n,i_1,i_2,i_3} = (u_{1,n} + i_1)\mathbf{a}_1 + (u_{2,n} + i_2)\mathbf{a}_2 + (u_{3,n} + i_3)\mathbf{a}_3$$

The Ewald real space sum for the binding energy of an ion at  $\mathbf{r}_k$  is given by

$$W_k^r = q_k \sum_{n=1}^{n_{\max}} q_n \sum_{i_1=i_{\min}}^{i_{\max}} \sum_{i_2=i_{\min}}^{i_{\max}} \sum_{i_3=i_{\min}}^{i_{\max}} \frac{\text{erfc}(|\mathbf{r}_k - \mathbf{r}_{n,i_1,i_2,i_3}|)}{|\mathbf{r}_k - \mathbf{r}_{n,i_1,i_2,i_3}|}$$

where

$$\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt$$

and the sums are carried out over all non-negligible terms. The index  $n$  varies over the ions of the unit cell, and the indices  $i_1$ ,  $i_2$ , and  $i_3$  describe the periodic translation of the unit cell along its principal axes.

The Ewald reciprocal lattice sum for the binding energy of an ion at  $\mathbf{r}_k$  is given by

$$W_k^f = \frac{-q_k}{V} \sum_{n=1}^{n_{\max}} q_n \sum_{m_1=m_{\min}}^{m_{\max}} \sum_{m_2=m_{\min}}^{m_{\max}} \sum_{m_3=m_{\min}}^{m_{\max}} \frac{\exp(-\frac{1}{2} |\mathbf{f}_{m_1,m_2,m_3}|^2 / \lambda^2)}{|\mathbf{f}_{m_1,m_2,m_3}|^2} \times \cos[2 \pi \mathbf{f}_{m_1,m_2,m_3} \cdot (\mathbf{r}_k - \mathbf{r}_{n,0,0,0})]$$

where the sums are carried out over all reciprocal lattice points for which the exponential is non-negligible.

The unit cell volume is given by  $V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$  and the coordinates in inverse lattice space are given by

$$\mathbf{f}_{m_1, m_2, m_3} = \begin{pmatrix} m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix}$$

The three reciprocal lattice vectors are given by

$$\mathbf{b}_j = \begin{pmatrix} b_{j1} & b_{j2} & b_{j3} \end{pmatrix}, \text{ where } \mathbf{b}_1 = \mathbf{a}_2 \times \mathbf{a}_3 / V \quad \mathbf{b}_2 = \mathbf{a}_1 \times \mathbf{a}_3 / V \quad \mathbf{b}_3 = \mathbf{a}_1 \times \mathbf{a}_2 / V$$

The Ewald term for the binding energy of an ion at coordinate  $\mathbf{r}_k = (x_k \ y_k \ z_k)$  by its own Gaussian of charge  $-q_k$  is given by

$$W_k^c = \frac{-q_k^2}{\sqrt{\epsilon}}$$

To determine the electrostatic potential  $V_{\mathbf{r}}$  at any point  $\mathbf{r}$ , a test charge  $q = 0$  is placed at that point (and similar infinitesimal charges are placed at corresponding points in all other unit cells) and the equations above reduce to

$$V_{\mathbf{r}} = \sum_{n=1}^N q_n \sum_{i_1=i_{\min}}^{i_{\max}} \sum_{i_2=i_{\min}}^{i_{\max}} \sum_{i_3=i_{\min}}^{i_{\max}} \frac{\text{erfc}(|\mathbf{r} - \mathbf{r}_{n,i_1,i_2,i_3}|)}{|\mathbf{r} - \mathbf{r}_{n,i_1,i_2,i_3}|} +$$

$$\frac{1}{V} \sum_{n=1}^N q_n \sum_{m_1=m_{\min}}^{m_{\max}} \sum_{m_2=m_{\min}}^{m_{\max}} \sum_{m_3=m_{\min}}^{m_{\max}} \frac{\exp(-2|\mathbf{f}_{m_1,m_2,m_3}|^2 / \epsilon)}{|\mathbf{f}_{m_1,m_2,m_3}|^2} \times$$

$$\cos[2 \mathbf{f}_{m_1,m_2,m_3} \cdot (\mathbf{r} - \mathbf{r}_{n,0,0,0})]$$

The details of the derivations have been described in a textbook<sup>14</sup> and in a recent review article<sup>15</sup>.

The relative convergence rates for the real space sums and the reciprocal lattice sums is controlled by  $\epsilon$ . For large values of  $\epsilon$  the Gaussian charge distribution is narrow and the inverse lattice sum converges more slowly. For small values of  $\epsilon$  the Gaussian charge distribution is wide and the real space sum converges more slowly. It is important that the summation limits for these sums are sufficiently large to guarantee convergence. When this condition is met, the sum  $W_k$  is independent of the value of  $\epsilon$ .

To convert the binding energy  $W_k$  from (electron charge)<sup>2</sup>/Å to eV, or the potential from electron charge/Å to V, multiply by 14.39976.

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